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16. ABSTRACT

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JOURNAL ARTICLE

Effects of Sediment Sorption and Abiotic Hydrolyses. 1. Organophosphorothioate Esters

Donald L. Macalady*[1] and N. Lee Wolfe

The kinetics of hydrolysis of selected organophosphorothioate insecticides were determined in sediment–water samples to define the role of hydrolysis in the sediment-sorbed state. Investigations with well-characterized sediments showed that the rates of neutral hydrolysis of chlorpyrifos [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate], diazinon [*O,O*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidyl) phosphorothioate], and Ronnel [*O,O*-dimethyl *O*-(2,4,5-trichlorophenyl) phosphorothioate] are unaltered when the compounds are sorbed to sediments. For chlorpyrifos, the observed rate constants were the same in the sediment and aqueous phases and similar in magnitude to those found for natural water samples. Limited data for diazinon and Ronnel indicated similar kinetic behavior for these related compounds. Alkaline hydrolysis rates in the sediment-sorbed phase for chlorpyrifos, on the other hand, were slowed considerably relative to those in the aqueous phase. Experiments indicated that the rate of alkaline hydrolysis in the sorbed state is approximately 10 times slower than in the bulk solution.

In sediment–water systems it is generally assumed that organic compounds do not hydrolyze in the sediment-sorbed state but that the compound is in rapid equilibrium between the sediment and aqueous phases and hydrolysis occurs only through the aqueous phase (Wolfe et al., 1977). Unfortunately, detailed studies to support such assumptions have not been reported in the literature. Thus, a quantitative expression describing the hydrolytic process in sediments, coupled with a mechanistic insight about sediment effects, is needed to evaluate the fate and transport of organic compounds in sediment and soil systems.

Recent linear free energy relationships (LFER) relate the sorption of nonionic organic compounds to the organic matter associated with the sediment (Karickhoff, 1981). Thus, the question arises as to what types of reactions can occur in this organic matrix. It is anticipated that different types of reactions would be affected differently. For hydrolysis reactions, a neutral hydrolysis reaction may be affected differently than an acid- or base-mediated reaction. Furthermore, recent studies suggest that relative to some degradative processes the assumption of a fast equilibrium between the sediment and water is not always valid (Karickhoff, 1980). Thus, the kinetics of sorption–desorption must be described and included in disappearance kinetic expressions.

Limited insight into reactions in the sorbed state is provided by studies addressing the breakdown of organophosphates and organophosphorothioates in soil systems. Unlike aqueous sediment suspensions, transport in the solid matrix of soil studies may be diffusion controlled and very slow. In soil studies, temperature, pH, moisture, and heavy metal effects have been reported (Sethunan and MacRae, 1969; Mingelgrin et al., 1977). Also, degradation is often divided into biotic and abiotic pathways by comparing sterile and nonsterile systems. In general, organophosphorus esters have been shown to undergo abiotic reactions in the soil sorbed states.

For studies of degradation of organic compounds in sediments, we selected three organophosphorothioate esters and designed experiments to test the hypothesis that hydrolysis occurred only in the aqueous phase, with no reaction of the esters in the sorbed phase. The three compounds were chlorpyrifos [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate], diazinon [*O,O*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidyl) phosphorothioate], and Ronnel [*O,O*-dimethyl *O*-(2,4,5-trichlorophenyl) phosphorothioate], selected because of the magnitude of their sediment–water partition coefficients (K_p) and neutral or alkaline hydrolysis rate constants. Experiments were designed to measure the rates of disappearance of these compounds in both the sediment-sorbed and the aqueous phases. Detailed studies were first carried out on

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chlorpyrifos and selected experiments were later carried out with diazinon and Ronnel.

EXPERIMENTAL SECTION

Instrumental. Most gas chromatographic (GC) analyses were performed by using a Tracor MT 222 gas chromatograph equipped with a ^{63}Ni electron capture detector and a 2 mm i.d. × 2 m long glass column packed with 10% SE-30 on 80–100 mesh Gas-Chrom Q. Operating conditions included injector, detector, and column oven temperatures of 215, 285, and 185–200 °C, respectively, and a N_2 carrier gas flow rate of 8 mL/min.

In several cases, interferences extracted from the sediments resulted in incomplete peak separations with the packed column. In these cases, GC analyses were conducted on a Hewlett-Packard (HP) 5840A gas chromatograph fitted with an HP 18835B capillary inlet system and an HP 18803B electron capture detector (ECD). The injector was equipped with a HP 18740-80210 fused quartz splitless liner. Chromatographic conditions were as follows: injector temperature, 210 °C; ECD temperature, 300 °C; isothermal oven temperature, 185 °C; helium carrier gas velocity, 33 cm/s (CH_2Cl_2 at 185 °C); nitrogen makeup gas flow, 20 mL/min. The column, also from HP, was a 50 m long, 0.32 mm i.d. fused silica capillary column coated with a 0.52-mm film of 5% phenylmethyl silicone.

Hydrogen ion activities were measured by using a Corning Model 112 pH meter equipped with an Orion catalog no. 9162 "ruggedized" pH probe for use in low ionic strength solutions. The probe was calibrated with commercially prepared buffers. In general, pHs determined in the stirred slurries used in our experiments did not differ significantly from those measured in the aqueous phases isolated by centrifugation from the slurries.

Chemicals. Chlorpyrifos, chlorpyrifos-oxon, and 3,5,6-trichloro-2-pyridinol were supplied by Dow Chemical Co. and were used without further purification. Structures were confirmed by gas chromatography–mass spectrometry (GC–MS) and nuclear magnetic resonance. All other solvents and chemicals used were used as commercially supplied reagent chemicals. Carbonate–bicarbonate buffer systems were employed to maintain constant pH for trials between pHs of 8 and 11.

Diazinon and Ronnel were used as supplied from the Pesticides and Industrial Chemicals Repository, USEPA, Research Triangle Park, NC 27711.

Purity checks on chlorpyrifos included melting point determination [43.0–43.2 °C observed, 42–43.5 °C literature (Brust, 1966)] and GC–MS analyses of a millimolar solution of chlorpyrifos in 33% methanol–water solution. No significant impurities were detected; in particular, chlorpyrifos-oxon and trichloropyridinol were present in less than 1.0 and 0.01% quantities, respectively.

Chlorpyrifos, diazinon, and Ronnel were introduced into reaction mixtures as saturated water solutions (Macalady and Wolfe, 1983). Concentrations of chlorpyrifos, diazinon, and Ronnel were determined in isooctane extracts of the experimental water solutions. For chlorpyrifos, the isooctane contained 5×10^{-8} M hexachlorobenzene (HCB) as an internal standard. For diazinon and Ronnel, the internal standard was 2×10^{-7} M of the methyl ester of (2,4-dichlorophenoxy)acetic acid (2,4-D-ME). Standard curves were linear ($r^2 > 0.99$) over the concentration ranges used in the experiments. Minimum working concentrations in isooctane solutions were 5×10^{-8} M chlorpyrifos, 1×10^{-7} M Ronnel, and 8×10^{-8} M diazinon.

Sediments used in this research were selected from a group of soils and sediments that were collected and characterized by Hassett et al. (1980). Sediment characteristics are summarized in Table I.

Table I. Characteristics of Sediments Used in These Studies

	sediment		
	EPA 14	EPA 23	EPA 26
pH (1:2)	4.3	7.1	8.1
CEC, mequiv/100 g	18.9	31.15	20.86
total N, %	0.064	0.195	0.152
organic carbon, %	0.48	2.38	1.48
sand:silt:clay, %	2:64:34	17:69:14	2:43:55
origin	WV Soil	Illinois River slough sediment	Mississippi River sediment
K_p for chlorpyrifos			
calcd from K_{ow}[a]	96	475	300
calcd from water solubility[a]	68	338	210
measured (±SD)	83 ± 6	403 ± 92	307 ± 96

[a] Hassett et al. (1980).

Kinetic Studies. Studies of the disappearance kinetics of chlorpyrifos from natural waters and of diazinon and Ronnel from distilled water were conducted according to procedures described elsewhere (Macalady and Wolfe, 1983).

Studies using sediment–water systems were all conducted in the following generalized pattern. Approximately equal quantities of air-dried sediment were added to each of 10–12 carefully cleaned 50-mL screw-top Corex centrifuge tubes. The mass of sediment in each tube was determined to the nearest milligram, and for experiments run under sterile conditions, the tubes and their contents were autoclaved twice for 30 min at 120 °C. Then, 25.0 mL of (sterile) aqueous pesticide solution, of known concentration, was added to each tube. For experiments at alkaline pHs, 1.0 mL of a 1.0 M carbonate–bicarbonate buffer was also added. The tubes were sealed with (Al-foil-lined) screw caps and placed on a wrist action shaker in a constant temperature chamber (25 °C for most runs).

After 1 h and at selected time intervals thereafter, individual tubes were analyzed as follows. The tubes and contents were centrifuged at 5700 rpm for 12 min in a Sorvall desk top centriguge. Then, 20.0 mL of the sediment-free aqueous solution was removed with a pipet and added to 5.0 mL of isooctane–internal standard; 1.1 mL was removed for a plate-count sterility check when appropriate. To the sediment and remaining water (3.9–5.0 mL) in the tube was added 5 mL of CH_3CN, after which the contents were thoroughly mixed on a vortex mixer. Further additions of 10.0 mL of distilled–deionized water and 5.0 mL of isooctane–internal standard were followed by a 12-h period of horizontal agitation on a flat-bed shaker. Finally, the tubes were sonicated for 1 h in a cooled water bath and refrigerated for phase separation and later analysis of the isooctane layer.

Two types of checks were made in order to determine that all of the ester had been extracted from the sediments. For initial samples, a material-balance check could determine whether all added material had been recovered. For other samples, the only recourse was to attempt to remove/extract additional material from the sediment by a more vigorous or lengthy extraction procedure. The procedure described proved adequate to remove within experimental error all added organophosphorothioate esters from the sediments used in this study.

Analysis by GC of the concentrations of esters in the isolated isooctane extracts enabled calculation of the concentrations of the ester in both the aqueous and the sediment phases as a function of time. In addition to providing kinetic information, these data enabled calcu-

Table II. Ranges of Measured Rate Constants for the Disappearance of Chlorpyrifos from Natural Water Samples at 25 °C

samples	rate constants[a]
Oconee River water (20)[b]	$(0.71–4.00) \times 10^{-5}$ min^{-1}
Hickory Hills Pond (12)[b]	$(1.00–3.90) \times 10^{-5}$ min^{-1}
EPA 14 supernatent (6)[b]	$(0.64–0.97) \times 10^{-5}$ min^{-1}

[a] Ranges shown represent a autoclaved and filter sterilized trials, along with trials involving nonsterilized waters. No bacterial effects are in evidence. Effects of pH are unimportant over the ranges observed in these waters. Metal catalysis is not a relevant factor. For a detailed analysis of the data including error analysis, see Macalady and Wolfe (1983). [b] Number of kinetic runs in parentheses.

lation of the ratio of the sediment concentration (mol/kg) to the water concentration (mol/kg). At sorptive equilibrium this becomes the equilibrium sediment to water concentration ratio, K_p.

In addition to degradation kinetic studies, several studies were designed to investigate the sorption process itself. In particular, the effect of pH on K_p was investigated. The methods used were similar in most details to those used in the kinetic studies, except that 15 tubes were used, 3 tubes each buffered in 5 different ways—at pH 4 with 1 mL of 0.02 M acetate–acetic acid, at pH 7 with 1 mL of 0.02 M phosphate, at pH 9 with 1 mL of 1 M carbonate–bicarbonate, at pH 11 with 1 mL of 1 M carbonate–bicarbonate, and unbuffered. Before each tube was sacrificed, the pH of the slurry was measured, with careful rinsing of the pH electrode using a minimum quantity of water. This was followed by immediate centrifugation and the remainder of the analytical procedure as described above.

RESULTS

Hydrolysis in Natural Water. The disappearance rate constants for chlorpyrifos in natural water samples were determined in order to compare such rates to distilled water values. The lack of significant biological contribution to chlorpyrifos degradation under these reaction conditions has already been reported (Macalady and Wolfe, 1983).

Table II summarizes the results of trials in which the first-order disappearance rate constants for chlorpyrifos were determined in samples from two North Georgia water bodies, the Oconee River and Hickory Hills Pond. The ranges of rate constants represent studies of samples taken at three different times over a period of about 1 year. Also shown in Table II is the range of rate constants determined in water isolated from a 20 g/L ($\rho = 0.02$) slurry of EPA 14, one of the sediments used in this study. The slurry had been stirred for 1 week, after which the water was isolated by centrifugation.

The values measured for the first-order disappearance rate constant, k_{obsd} (Table II) show considerable varation but are uniformly greater than the distilled water value of $(6.2 \pm 0.9) \times 10^{-6}$ min^{-1} (Macalady and Wolfe, 1983). The variations have no obvious relationship to time of sampling, pH, sterility, or method of sterilization (filtration through 0.22-μm Nucleopore filters or autoclaving). Effects of sorption to container walls have been accounted for in the reported values. Because no chlorpyrifos-oxon was detected, oxidation was not indicated as the source of this variation.

The possibility of metal ion catalysis was considered, and metal ion concentrations were measured in all reaction solutions (Al, Ca, Fe, Mg, Zn, Cu, Ni, and Mn, as determined by plasma emission spectroscopy). Copper catalysis is known for chlorpyrifos (Mortland and Raman, 1967; Blanchet and St. George, 1982). By extrapolation of the rate enhancements by copper reported by Blanchet and St. George (1982), one can easily show that the levels of metals present in these, and, indeed, in most, natural waters are about an order of magnitude lower than those necessary to provide a measurable enhancement of the (neutral) hydrolysis rate. Effects of Zn, Ni, Co, Al, Ca, and Mg can also be eliminated (Mortland and Raman, 1967).

Thus, the variations in disappearance rate constants of chlorpyrifos in natural water samples by a factor of up to 7 times the distilled water value are of unexplained origin (Macalady and Wolfe, 1983).

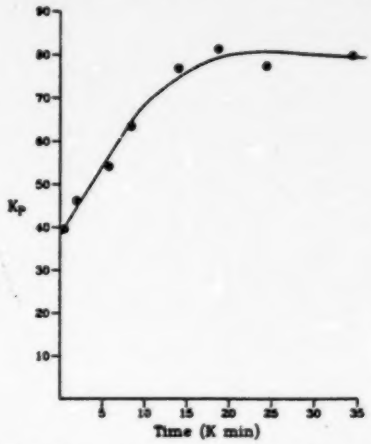

Figure 1. Plot of measured K_p vs. time for the partitioning of chlorpyrifos to EPA 14 sediment in a sediment–water system ($\rho = 0.2$).

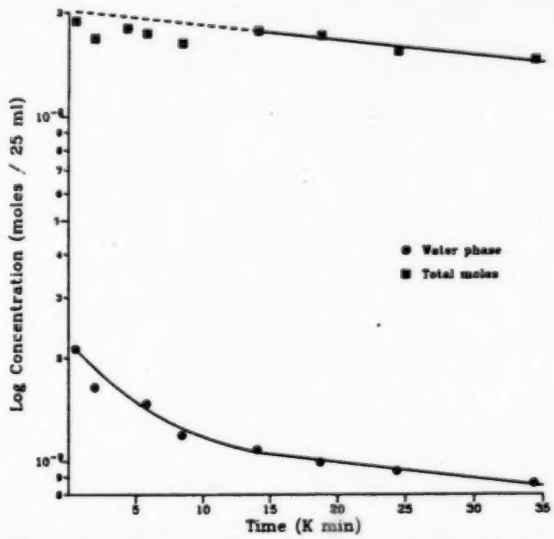

Figure 2. Log concentration vs. time for the hydrolysis of chlorpyrifos in EPA 14 sediment–water system at pH 4.

Sediment–Water Studies: Neutral Hydrolysis. Figure 1 is a plot of sediment concentration–water concentration of chlorpyrifos, labeled as K_p, vs. time (labeled in units of 10^3 min) in EPA 14 sediment using a sediment to water mass ratio (ρ) of 0.2. Figures 2 and 3 show plots of natural log concentration vs. time data for the disappearance of chlorpyrifos from EPA 14 and EPA 23 sediment–water systems, respectively, at near neutral pHs and constant temperature (25 °C). The figures illustrate that after an initial period of time for sediment–water equilibrium, the disappearance kinetics are pseudo first order in both phases.

Table III. Observed and Calculated Values of Rate Constants (min^{-1}) for Chlorpyrifos in Sediment-Water Systems at Nonadjusted pHs[a]

	sediment			
no.	EPA 14	EPA 14	EPA 23	EPA 23
sediment/water (ρ)	0.012	0.20	0.016	0.016
fraction sorbed	0.51	0.94	0.87	0.87
sterile?	yes	yes	no	yes
k_{obsd}	1.9×10^{-5}	1.0×10^{-6}	1.7×10^{-5}	1.6×10^{-5}
k_{obsd} (calculated)[b]	4.9×10^{-6}	6.0×10^{-7}	1.3×10^{-6}	1.3×10^{-6}
k_i		$(6 \pm 2) \times 10^{-5}$	$(4 \pm 1) \times 10^{-5}$	$(4 \pm 1) \times 10^{-5}$
k_o		$(6 \pm 2) \times 10^{-4}$	$(9 \pm 3) \times 10^{-4}$	$(4 \pm 2) \times 10^{-4}$
k_w (fixed)[c]		1.0×10^{-6}	1.0×10^{-6}	1.0×10^{-6}
k_s		$(6.9 \pm 0.9) \times 10^{-6}$	$(1.8 \times 0.1) \times 10^{-5}$	$(1.2 \times 0.1) \times 10^{-5}$
pH (H_2O phase)		4.1 ± 0.4	7.2 ± 0.2	7.4 ± 0.4

[a] See Figure 4 for symbol definitions. [b] Assuming sediment–water equilibrium, no hydrolysis in sorbed state, and $k_w = 1 \times 10^{-6}$, $k_{obsd} = k_w/(1 + K_p)$. [c] For computer model calculations.

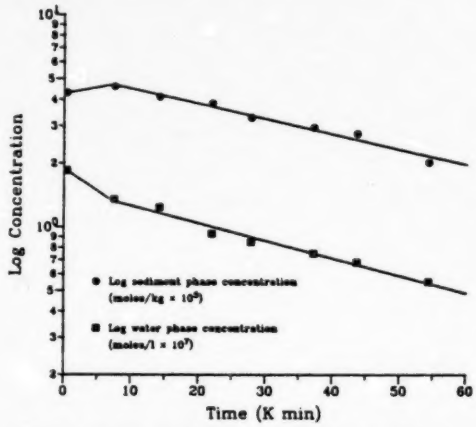

Figure 3. Log concentration vs. time plots for the disappearance of chlorpyrifos in the water phase and in the sediment-sorbed phase in an EPA 26 sediment–water system at pH 7.3 with 87% ester sorbed at equilibrium.

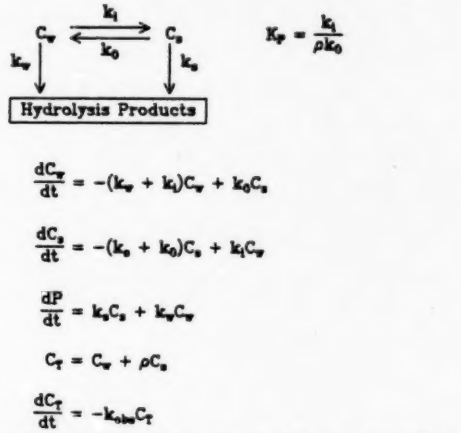
Hydrolysis Products
$K_p = \frac{k_i}{\rho k_o}$
$\frac{dC_w}{dt} = -(k_w + k_i)C_w + k_o C_s$
$\frac{dC_s}{dt} = -(k_s + k_o)C_s + k_i C_w$
$\frac{dP}{dt} = k_s C_s + k_w C_w$
$C_T = C_w + \rho C_s$
$\frac{dC_T}{dt} = -k_{obs} C_T$

Figure 4. A kinetic model to describe the hydrolysis of chlorpyrifos in sediment–water systems. The sediment–water partition coefficient is given by $K_p = k_i/\rho k_o$, and the amount of chlorpyrifos in the system is given by $C_T = C_w + \rho C_s$.

Values for neutral hydrolysis rate constants of chlorpyrifos were determined based on the scheme shown in Figure 4. Experimentally determined water concentrations (C_w), sediment concentrations (C_s), product concentrations (P, obtained by difference), and observation times (minutes) were used along with the differential equations in a computer program (Knott and Reece, 1977) that calculated best fit values for any three of the four rate constants (k_i, k_o, k_w, k_s). For purposes of the fit, a value of $k_w = 1 \times 10^{-6}$ min^{-1} (the hydrolysis rate constant with the sediment removed) was given to the program as a "known" value.

The value 1×10^{-6} min^{-1} represents a typical value found for chlorpyrifos disappearance rate constants in natural waters or waters isolated from slurries of the sediments used in the study (see Table II). It is also a value obtained from a plot of the log C_w vs. time data from the EPA 14 $\rho = 0.2$ study (Figure 2). The value calculated from the EPA 23 studies (Figure 3) is 1.9×10^{-5} min^{-1}.

Table III summarizes the results of the data analysis of sediment–water studies of chlorpyrifos degradation at 25 °C. Included are the results from a less detailed study using EPA 14 where only disappearance of the ester from the total system was monitored.

Neutral hydrolysis disappearance rate constants for diazinon and Ronnel were determined at 35 °C in a single study with an EPA 26 sediment–water system. K_p's were measured at times greater than 2000 min.

At 35 °C, diazinon has a first-order-rate constant in distilled water of $(1.2 \pm 0.2) \times 10^{-6}$ min^{-1}, whereas the value for Ronnel is $(2.0 \pm 0.2) \times 10^{-5}$ (Wolfe et al., 1983).

Table IV. Experimental Values for Neutral Hydrolysis Disappearance Rate Constants (min^{-1}) in an EPA 26 Sediment–Water System for Diazinon and Ronnel at 35 °C[a]

	diazinon	ronnel
sediment/water (ρ)	0.040	0.040
fraction sorbed	0.64	0.96
k_{obsd}	$(3 \pm 1) \times 10^{-5}$	$(2.7 \pm 0.4) \times 10^{-5}$
k_{obsd} (calculated)[b]	1.3×10^{-5}	2.3×10^{-6}
k_w (distilled)	$(1.2 \times 0.2) \times 10^{-5}$	$(2.0 \pm 0.2) \times 10^{-5}$
k_w (observed)	$(3.8 \pm 0.6) \times 10^{-5}$	$(3.8 \pm 1.8) \times 10^{-5}$
k_s (observed)	$(2.9 \pm 0.5) \times 10^{-5}$	$(2.6 \pm 0.3) \times 10^{-5}$

[a] Symbols defined in Figure 3. [b] Assuming sediment–water equilibrium, no hydrolysis in the sorbed state, and $k_w = 3k_w$ (distilled) (see Discussion), k_{obsd} (calculated) = $3k_w$ (distilled)/$(1 + \rho K_p)$.

The experimental system used for the diazinon–Ronnel study was initially sterile, but sterility had been lost in most tubes by the time they were sacrificed (plate counts gave about 10^5 cells/L).

Rate constants for the neutral hydrolysis of diazinon and Ronnel were calculated from the slopes of ln C_w and ln C_s vs. time plots rather than from computer calculations based on the model in Figure 4. Values obtained from this study are shown in Table IV along with auxiliary data concerning the experiment.

Alkaline Hydrolysis. To provide preliminary information on hydrolysis at alkaline pHs in sediment–water systems, the effects of pH on sorption were investigated by using EPA 26. The results are presented in Table V.

Table V. K_p as a Function of Time at Five Different pHs for Chlorpyrifos on EPA 26, $\rho = 0.015$

	K_p					
	pH 5.5[a]	pH 7.2	pH 7.2[b]	pH 9.2	pH 10.8	av ± SD
180 min	233	214	189	198	213	209 ± 17
1175 min	284	264	246	216	224	247 ± 28
2610	349[c]	303	225	223	249	250 ± 37

[a] Ranged from 4.7 to 6.1, buffer inadequate. [b] Unbuffered. [c] There is reason to believe that this value is in error. The material balance was incorrect.

Alkaline hydrolysis experiments were conducted for chlorpyrifos in EPA 23 and EPA 26 sediment–water systems. In addition, the data at pH 10.8 from the pH–K_p study were also used in a more limited way.

Using EPA 26, two similar experiments were conducted at a pH of 10.6. In one, the pH adjustment was made immediately after adding the chlorpyrifos solution to the sediment. (This had also been the case in the EPA 23 study and the pH–K_p study.) In the other EPA 26 study, however, the chlorpyrifos solution and sediment were allowed to equilibrate at room temperature for 3 days (4450 min) prior to addition to chlorpyrifos.

The results of the three trials without sediment–chlorpyrifos preincubation are summarized in Table VI. The information presented in this table is similar to that presented in Table III and the values of k_i, k_o, and k_s were calculated by using the same kinetic model (Figure 4) and the same computer program (Knott and Reece, 1977). The fixed values of the aqueous pseudo-first-order rate constant, k_w, were calculated from the experimental pHs and the pH–rate profile for chlorpyrifos in buffered distilled water (Macalady and Wolfe, 1983). The same fixed values of k_w were used to arrive at the values of k_{obsd} (calculated).

Figure 5 is a graphical presentation of the data from the study involving sediment–chlorpyrifos incubation for 3 days prior to pH adjustment.

DISCUSSION

The purpose of the reported experiments was to test the hypothesis that hydrolysis reactions are quenched for molecules that are in the sediment-sorbed phase in sediment–water systems. The results strongly indicate, at least for organophosphorothioate esters, that the hypothesis is valid for alkaline-catalyzed hydrolysis reactions and invalid for neutral hydrolysis reactions.

One of the difficulties inherent in testing the above hypothesis is treating the sorption–desorption kinetics in the disappearance rate expression. If, for example, hydrolysis does not occur in the sediment sorbed state and desorption rate is much slower than the aqueous hydrolysis rate, the observed kinetics would be expected to be controlled by initial disappearance of the aqueous esters, followed by a much slower, desorption-controlled disappearance rate.

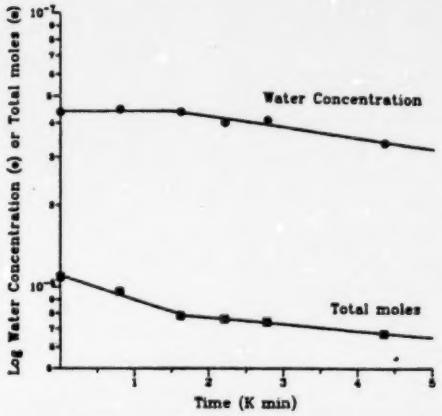

Figure 5. Plots showing the degradation of chlorpyrifos at pH 10.6. Samples were equilibrated at pH 8 for 3 days followed by a pH jump to 10.6.

The kinetic approach to sorptive equilibrium shown in Figure 1 for the chlorypyrifos–EPA 14 system with a sediment to water ratio of 0.2 contains a relatively rapid and a much slower component. The kinetic plots for the neutral hydrolysis of chlorpyrifos for this system, shown in Figure 2, demonstrate that first-order disappearance kinetics are not operative until sorptive equilibrium is reached (15 000 min).

The linearity of the plot after 15 000 min, however, suggests that the sorption-desorption process is faster than neutral hydrolysis. In order to substantiate this, the kinetics of sorption–desorption was built into our model for the overall kinetics of the experimental system (Figure 4).

The calculated values for sorption and desorption rate constants, k_i and k_o, shown in Table III, are consistent with this conclusion for neutral hydrolysis. Sorption kinetics are not fast, however, in comparison to the alkaline hydrolysis rates of chlorpyrifos at the pHs employed in our studies (Table VI).

Thus, the discussion below for neutral hydrolysis assumes that sorption–desorption kinetics are fast relative to hydrolysis. For the alkaline hydrolysis case, however, the role of sorption kinetics will be addressed in the analysis of the experimental results.

Neutral Hydrolysis. If hydrolysis does not occur in the sorbed state and sorptive equilibrium is fast relative to hydrolysis, the overall disappearance rate constant should be given by the water phase hydrolysis rate, k_w,

Table VI. Experimental and Calculated Values of the Rate Constants for the Alkaline Hydrolysis of Chlorpyrifos in Sediment–Water Systems[a]

	EPA 23	EPA 26	EPA 26
pH	10.67 ± 0.04	10.60 ± 0.04	10.85 ± 0.05
ρ	0.019 ± 0.001	0.031 ± 0.001	0.016
K_p	453 ± 59	191 ± 4	229 ± 18
av fraction sorbed	0.90	0.85	0.78
k_{obsd}	$(1.05 \pm 0.11) \times 10^{-4}$	$(1.10 \pm 0.04) \times 10^{-4}$)	$(1.81 \pm 0.04) \times 10^{-4}$
k_{obsd} (calculated)[b]	5.0×10^{-5}	6.2×10^{-5}	1.3×10^{-4}
k_i	$(1.3 \pm 0.8) \times 10^{-3}$	$(2.5 \pm 0.9) \times 10^{-2}$	—[c]
k_o	$(1.8 \pm 1.1) \times 10^{-4}$	$(4.4 \pm 1.7) \times 10^{-3}$	—[c]
k_w (fixed)[d]	4.8×10^{-4}	4.3×10^{-4}	6.3×10^{-4}
k_s	$(7.1 \pm 0.8) \times 10^{-5}$	$(4.1 \pm 0.3) \times 10^{-5}$	—[c]

[a] Symbols defined in Figure 4. No preequilibrium between sediment and chlorpyrifos prior to pH adjustment. [b] Assuming sediment–water equilibrium, no hydrolysis in the sorbed state, and k_{obsd}(calculated) $= k_w/(1 + PK_p)$. [c] Insufficient data for computer model calculations. Data from K_p–pH study. [d] For computer calculations. The value of k_w is the expected distilled water hydrolysis rate constant at this pH. See the text.

times the fraction of ester in the water phase, or (Karickhoff, 1980)

$$k_{obsd} = k_w \frac{1}{\rho K_p + 1} \quad (1)$$

where ρ is the sediment to water mass ratio (unitless), K_p is the sediment–water partition coefficient, and k_w is the (neutral) hydrolysis rate constant in the aqueous phase.

For chlorpyrifos, the predicted overall disappearance rate constants based on this hypothesis, shown as k_{obsd} (calculated) in Table III, are all considerably lower than the experimental values for k_{obsd}. The differences vary from a factor of 3.9 for the preliminary experiment with only 51% of the chlorpyrifos sorbed (to EPA 14) to 17 for about 90% sorbed.

These constants are calculated based on a value of 1.0×10^{-5} min^{-1} for k_w. This value was selected, as discussed above, as a reasonable expectation of the disappearance rate constant in the aqueous phase of the sediment–water systems. However, even with the largest disappearance rate constant observed for a natural water ($k_w = 4.0 \times 10^{-5}$ min^{-1}, Table II), the observed rate constants in experiments with 87–94% of the chlorpyrifos sorbed are considerably faster (by factors of 3–4) than predicted by a model assuming no hydrolysis in the sorbed state.

Values for the disappearance rate constant for diazinon and Ronnel in natural waters have not been reported, although these rates might be expected to be 2–4 times greater than the distilled water values, as was the case for chlorpyrifos. When a value of k_w equal to 3 times the distilled water value is assumed, the rate constant calculated for Ronnel (eq 1) assuming no sorbed-state hydrolysis is 12 times slower than the observed overall disappearance rate constant.

For diazinon, the observed rate constant is only a factor of 2.3 larger than the value obtained by assuming no hydrolysis in the sorbed phase. Because only 64% of the diazinon was sorbed, this difference is less definitive than for situations where a greater fraction of the ester is sorbed. Also, biodegradation may have complicated the diazinon results. Unlike chlorpyrifos and Ronnel (Steen, 1982), diazinon has been reported (Sharom et al., 1980) to undergo biologically mediated degradation under similar experimental conditions.

On the basis of these observations, it is apparent that either hydrolysis is occurring in the sorbed state or some type of heterogeneous catalysis by the sediments is operative. It is not possible based upon our experimental evidence to unambiguously distinguish between these two possibilities. Further consideration of the calculated and observed values for the sediment-sorbed hydrolysis rate constants does, however, provide strong indication that the operative mechanism is neutral hydrolysis of the sorbed ester—not heterogeneous catalysis.

For chlorpyrifos, the values of k_s (Table III) are from computer calculations based on the model shown in Figure 4. These values of k_s are in all three cases similar to values calculated from the slopes of ln C_s vs. time plot (data not shown). In each case the calculated value of k_s was close to the value of k_w used in the model calculations. The k_s values are also of similar magnitude to the values of k_w calculated from ln C_w vs. time plots for the same experiments (see Results).

For diazinon and Ronnel, the same similarities in rate constants are observed. The experimental (from ln C vs. time plots) values of k_w and k_s are in close agreement.

Thus, the preferred conclusion is that neutral hydrolysis of organophosphorothioate esters proceeds at similar rates in both the aqueous and sediment-sorbed phases of the sediment–water systems as opposed to a heterogeneous catalytic effect by the sediment. This conclusion is strengthened by the fact that the results reported represent three different esters, three different sediments, and sediment to water ratios that vary by a factor of 12. The general validity of this conclusion for other classes of hydrophobic molecules is supported by data already reported for hexachlorocyclopentadiene (Wolfe et al., 1982) by results for 4-(*p*-chlorophenoxy)butyl bromide and benzyl chloride (Pierce and Wolfe, 1984) and by the absence of heterogeneous catalysis by sediments in the hydrolysis of esters of (2,4-dichlorophenoxy)acetic acid (Macalady and Wolfe, 1984).

Alkaline Hydrolysis. A preliminary consideration for these studies is the effect of pH on the extent and rate of the sorption process. The data in Table V show there is no substantial effect of pH on the equilibrium sorption partition coefficient of chlorpyrifos to EPA 26. Also, the K_p measured at pH 10.67 for chlorpyrifos and EPA 23 (Table VI) agrees within experimental uncertainty to the K_p's observed at neutral pH (Table I). Likewise, the effect of pH on sorption–desorption kinetics also appears to be minor. Calculated values for k_o and k_i for EPA 23–chlorpyrifos are similar at pHs of 4.1 and 10.67 (Tables II and VI).

The disappearance of chlorpyrifos in sediment–water systems in which pH adjustment was made immediately after addition of the chlorpyrifos to the sediments gave plots of ln concentration that were linear vs. time through two half-lives for both the sediment-sorbed and aqueous phases. The computer fit of the data to the model shown in Figure 4 is quite good, as illustrated by the calculated uncertainties shown for k_i, k_o, and k_s in Table VI. Note that in these experiments, the sorption–desorption rate constants were calculated to be similar in magnitude to the aqueous hydrolysis rate constants.

In constrast to the neutral hydrolysis case, the calculated values for k_s for alkaline hydrolysis are 7–11 times smaller than the aqueous hydrolysis rate constants. Also, the observed overall disappearance rate cosntants are considerably lower than the aqueous phase rate, and the overall disappearance rate constants calculated by assuming no sorbed-phase hydrolysis are much closer to the observed values than was the case for neutral hydrolysis.

Thus, the conclusion is that alkaline hydrolysis, unlike neutral hydrolysis, is considerably retarded in rate when the chlorpyrifos is in the sediment-sorbed phase. A similar retardation of the alkaline hydrolysis rate constant of the *n*-octyl ester of (2,4-dichlorophenoxy)acetic acid in the sorbed phase of sediment–water systems has been reported by Macalady and Wolfe (1984).

The alkaline hydrolysis of chlorpyrifos in an ester–sediment–water system that had been aged for three days prior to pH adjustment (Figure 5) is somewhat different from the case without preequilibration. For chlorpyrifos–EPA 26, unlike the EPA 14 system shown in Figure 1, 3 days is ample time for the achievement of equilibrium between the aqueous and sorbed state.

Though the data from this experiment are quite limited, there appears to be an initial disappearance of the total ester characterized by a rate constant (2.3×10^{-4} min^{-1}, calculated based on the first three points in Figure 5) similar to those observed in the experiments without preequilibration. This is followed by a much slower ($k_{obsd} = 5 \times 10^{-5}$ min^{-1}) disappearance at later times.

Clearly, the precise nature of these sorption–desorption processes are unknown, and a better understanding is

needed before a more complete picture of the role of sediments in the kinetics of aqueous chemical reactions can be formulated.

CONCLUSIONS

Neutral hydrolysis studies show that for three organophosphorothioate esters hydrolysis occurs in the sediment-sorbed phase of sediment–water samples. The hydrolysis reactions in the sediment-sorbed phase has the same neutral hydrolysis rate constant (within experimental error) as that in the aqueous phase of the sediment–water systems. Thus, in pollutant fate modeling, the neutral hydrolysis process can be simulated by assuming equilibrium between the aqueous and sediment phase with hydrolysis occurring in both phases with the same disappearance rate constant.

In contrast, the alkaline hydrolysis of chlorpyrifos does not occur in the sediment-sorbed phase with a rate constant comparable to that of the aqueous phase. For describing the fate of organophosphorothioate in sediments, a model with partitioning of the ester to the sediment with reaction in the aqueous phase only is adequate. Further studies with these esters are needed, however, to evaluate the effect of pH and incubation time on this process.

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Registry No. Chlorpyrifos, 2921-88-2; diazinon, 333-41-5; ronnel, 299-84-3.

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